INVESTIGATION OF THE MAGNETIC FLUID
MASS TRANSFER IN POROUS MEDIA

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Introduction. Variety of physical effects of the mass transfer process in porous media can be described by the equations of irreversible thermodynamics [1]. It is possible to employ the Onsager’s assumption of linear dependence of the mass flow on corresponding force gradients at small deviation from the equilibrium state. Some phenomenological laws exist, which linearly describe the irreversible physical processes. If two or more of these phenomena take place simultaneously, they overlay and cause new effects. By substitution of dissolved substance molar mass with the mass of colloidal particle, it is possible to describe the transfer processes with the same molecular-kinetic equations as those of molecular solutions. The magnetic fluid is identified as a binary solution and the thermodynamics of irreversible processes is employed to describe the mass transfer processes in porous media in this investigation. The changes in composition and structure in the boundary layers of porous media affect not only the flow velocity but cause some additional effects: capillary osmosis – a mass flow under the influence of diluted substance gradient \( \nabla C \), thermoosmosis – a flow under the influence of temperature gradient \( \nabla T \), electroosmosis – a flow under the influence of electric field gradient \( \nabla E \). These effects may be expressed separately or as associated phenomena of filtration flow. This is the reason why the mass transfer processes in porous media must be solved taking into account the combined action of all gradients. Consequently, it is necessary to take into account the mass fluxes of different components of the solution as well as the flux of energy and the electric charge.

1. The experimental set-up. The transfer phenomena of a two component flow through the porous media are investigated using an experimental system which consists of two reservoirs separated by a porous membrane. The experimental set-up (Fig. 1) consists of two equal \( W = 2.65 \text{ cm}^3 \) cylindrical thermo-stated volumes made of brass. The volumes are divided by porous media, which consist of five chemically stable polymer membranes with the following characteristics: porosity \( K = 78–83\% \), average diameter of a pore \( d_e = 0.951–1.05 \text{ m} \), thickness of one membrane \( l = 151.4 \text{ m} \). The constant pressure gradient on the membrane is provided by a special system which consists of an argon balloon and two pressure reducers.

The studied MF samples were prepared by a coprecipitation method according to the technology described in details in [2]. The magnetic nanoparticles of Fe₃O₄ were coated with oleic acid and suspended in tetradecane. The particles were washed three times with acetone (pure, for analysis) prior to their dispersion in the carrier liquid. This procedure removes any excess of oleic acid (free), which may occur during the preparation. The volume concentration of the magnetic phase was determined by density-metric measurements: \( \varphi (\rho - \rho_0) / (\rho_m - \rho_0) \), where \( \rho \), \( \rho_m \), \( \rho_0 \) are the densities of MF, solvent and magnetic material, respectively.

The flow rates of heat and mass through the porous membrane upon the gradients of pressure and concentration are investigated by measuring the spontaneous magnetization \( L \sim C \sim \varphi \) (\( C \) is the molar concentration of particles) of the magnetic fluid in cell volumes. Magnetic measurements were performed using the

\[ \text{http://www.ipul.lv/pamir/} \]
Fig. 1. The set-up of the mass transfer experiment: 1 – brass material; 2 – cooling jacket; 3 – porous membrane; 4 – magnetic liquid; 5 – teflon material; 6 – water inlet.

vibrating sample magnetometer [3]. The spontaneous magnetization is defined by the measurements of fluid magnetization.

2. Description of the problem. The system is closed as there is no mass exchange between the experimental cell and the surrounding. The characteristics of substances are considered to be equal in each reservoir. The changes of pressure $\Delta P$ and concentration $\Delta C_k$ take place only in the membrane. The increasing of entropy $S$ in such system is a result of irreversible processes inside the cell:

$$T \frac{dS}{dt} = \sum I_k X_k = - \sum I_k \Delta \mu_k ,$$

$I_k$ is the mass flux of the component $k$ through the diaphragm ($k = 1$ – dispersion medium, $k = 2$ – disperse medium), $X_k$ – thermodynamic strength, $\mu_k$ – chemical potential.

$$\Delta \mu_k = (\partial \mu_k / \partial P) \Delta P + \Delta_p \mu_k = v_k \Delta P + \Delta_p \mu_k$$

$$\Delta_p \mu_k = (\partial \mu_k / \partial C)_P \Delta C_k ,$$

$v_k$ – partial volume of the component $k$. The volume velocity – $J = - \sum I_k v_k$

$$T \frac{dS}{dt} = J \Delta P + \sum I_k \Delta_p \mu_k$$

According the Gibbs–Duhem theorem, $\sum C_k \Delta_p \mu_k = 0$. The thermodynamics of irreversible processes proves the invariance of entropy producing $dS/dt$ a linear transformation of fluxes:

$$\sum I_k \Delta_p \mu_k = \sum I_k^* \Delta_p \mu_k ,$$

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where \( I_i^3 = I_k - C_i V \); \( V \) is the average barometric velocity. Basing on entropy production and substituting (2) in (1), one gets:

\[
I_1^3 = \alpha_{11} \Delta P \mu_1 + \alpha_{12} \Delta P \mu_2 + \alpha_{13} \Delta P \\
I_2^3 = \alpha_{21} \Delta P \mu_1 + \alpha_{22} \Delta P \mu_2 + \alpha_{23} \Delta P \\
V = \alpha_{31} \Delta P \mu_1 + \alpha_{32} \Delta P \mu_2 + \alpha_{33} \Delta P
\]

According to the Onsagers theorem:

\[
\alpha_{12} = \alpha_{21}; \quad \alpha_{23} = \alpha_{32}; \quad \alpha_{13} = \alpha_{31}.
\]

Capillary osmosis may be characterized as a flow, which is caused by the gradients of chemical potentials if \( \Delta P = 0 \). In this case the volume velocity may be expressed using (9) and Onsagers expressions (6):

\[
V = \alpha_{13} \Delta P \mu_1 + \alpha_{23} \Delta P \mu_2.
\]

Values of the coefficients \( \alpha_{13} \) and \( \alpha_{32} \) are calculated from the known averaged characteristics of the membrane, investigated fluids and determined experimentally from expressions (3) and (4) by measuring mass flux rates of tetradecane and magnetic fluid through the membrane at \( \Delta P = \) constant:

\[
\alpha_{13} = (I_1^3/c) \times (\Delta P)^{-1}; \quad \alpha_{23} = (I_2^3/c) \times (\Delta P)^{-1} \\
V = [(I_1^3/c) \Delta P \mu_1 + (I_2^3/c) \Delta P \mu_2] \times (\Delta P)^{-1}
\]

3. Experimental results and discussion. Considering that all pores are cylindrical with an approximately equal radius, it is possible to calculate \( \alpha_{13} \) from the Darcy’s law: \( \alpha_{13} = (\mu \cdot r_c^2)/(8\eta V^2 n) \), where \( n \) denotes porosity, \( r_c \) is the radius of pores, \( \eta \) is the viscosity, \( v_m \) is the molar volume of tetradecane. The following characteristic values of tetradecane are obtained: \( \alpha_{13} = 1.59 \times 10^{-4} \) (mole)/(N·m⁻³) at the temperature 293 K and \( \alpha_{13} = 1.24 \times 10^{-4} \) (mole)/(N·m⁻³) at the temperature 283 K. On the other hand, experiment gives following values \( \alpha_{13} = 2.9 \times 10^{-5} \) (mole)/(N·m⁻³) and \( \alpha_{23} = 2.28 \times 10^{-6} \) (mole)/(N·m⁻³) at the temperature 285 K. The osmotic pressure difference between magnetic fluid and tetradecane was measured by the osmometer and was found to be \( \Delta P = 227.36 \) N m⁻². It yields: \( \Delta P \mu_1 = v_m \Delta P = 260.5 \times 10^{-6} \) m³ mole⁻¹ \times 227.36 N m⁻² = \( 5.92 \times 10^{-7} \) J mole⁻¹, \( \Delta P \mu_2 = RT \Delta C/C_0 = 8.31 \) J mole⁻¹ K⁻¹ \times 285 K \times 1 mol m⁻³ \times 1.51 \times 10⁻¹ m³ mole⁻¹ = 3.58-10² N m⁻¹. Substituting the values into equation (9), one obtains:

\[
V = (2.9 \times 10^{-5} \times 5.92 \times 10^{-2}) + (2.28 \times 10^{-6} \times 3.58 \times 10^2) = \]
\[= -1.77 \times 10^{-4} + 8.16 \times 10^{-4} = 6.39 \times 10^{-4} \text{ mole m}^{-2} \text{s}^{-1} = \]
\[= 6.39 \times 10^{-4} \times 2.6 \times 10^{-4} = 1.6 \times 10^{-7} \text{ m}^3 \text{ m}^{-2} \text{s}^{-1}.
\]

Concentration variations in the cell are caused not only by the osmotic flow of fluid but also by the forretic transport and transport by diffusion \( Q \) of particles.

\[
Q = \alpha_{23} \Delta P \mu_1 + \alpha_{22} \Delta P \mu_2 = -\alpha_{23} \Delta P v_m + \alpha_{22} \Delta P \mu_2.
\]

In this case, \( \alpha_{23} \) characterizes the mass flow of particle \( Q = \alpha_{23} \Delta \mu_1 \) under the action of osmotic pressure difference \( \Delta P = -\Delta \mu_1/v_m \), where \( \alpha_{22} \) is a diffusion coefficient of particles. The diffusion coefficient was determined from the Stokes equation \( D = kT/3\pi m d \) (\( k \) is the Boltzman constant, \( d \) is the diameter of a particle) and was found to be small: \( D = 2 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \). Neglecting the small
part of diffusion mass transfer, one obtains $Q = -2.28 \cdot 10^{-6}$ (mole)$^2$N$^{-1}$m$^{-3}$s$^{-1}$ × 227.4N m$^{-2}$ × 260.5$\cdot$10$^{-6}$ m$^3$mole$^{-1} = -1.345\cdot10^{-8}$ mole m$^{-2}$s$^{-1} = -2.03\cdot10^{-9}$ m$^3$mole$^{-1}$s$^{-1}$.

Fig. 2 shows the concentration changes in time in the cell volumes filled with the magnetic fluid (volume 1) and tetradecane (volume 2). In the initial state the osmotic pressure is maximal and the change in concentration is relatively rapid. The process saturates and reaches equilibrium in approximately 100 hours. The concentration changes in the cell may be characterized by the equation:

$$\frac{\partial C}{\partial t} = (V - CQ) \times \left( \frac{S}{W} \right)$$  \hspace{1cm} (10)$$

The first differential may be approximated by $(\partial C/\partial t) \approx \Delta C/\Delta t$ at the initial stage of the process. Fig. 2 gives $\Delta C/\Delta t = 1.18 \cdot 10^{-7}$. Using the experimentally obtained values of $V$ and $Q$, one gets $\Delta C/\Delta t = 4 \cdot 10^{-7}$. Some difference in these values probably is connected with the rapid changes of the osmotic pressure. $\Delta C/\Delta t$ are evaluated after 8 hours.

Fig. 3 illustrates the distribution on the nanoparticle size ($m_i \sim d$ is the magnetic moment of a particle) after passing through the porous membrane during different periods of time. TD-50 is the initial probe of the magnetic fluid. Tetrad. is the probe of pure tetradecane, where to the magnetic particles penetrate through the porous membrane after 284 hours. TD-31 is a TD-50 probe but after 284 hours when a number of nanoparticles are transferred through tetradecane. TD-40 is the initial TD-50 probe filtrated through the membrane during 2200 s at the pressure 1401 N m$^{-2}$.

REFERENCES